

Reactivity 3.4 · Electron-pair sharing reactions

International Baccalaureate · IB Diploma · Chemistry · HL

Scope and prerequisites

This handout covers selected HL/SL topics for the course first assessed in 2025; it is not the whole syllabus.

Prerequisites: covalent bonding and polarity from Structure 2.2, alkenes and halogenoalkanes from Structure 3.2, and radical (electron-sharing) mechanisms from Reactivity 3.3.

The examples are original and fictional: they are not real measurements or real student investigations.

Electron-pair sharing reactions

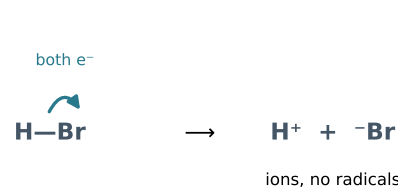
■ What would explain this observation?

- Bromoethane shaken with warm sodium hydroxide solution turns into ethanol, while the same alkane skeleton with no C–Br bond ignores the hydroxide completely. What does the C–Br bond make possible?

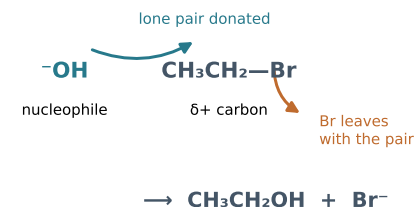
■ Build the model

- A covalent bond can also break by **heterolytic fission**: BOTH electrons of the shared pair move to one atom, forming ions. A double-barbed curly arrow shows an electron PAIR moving.
- A **nucleophile** is an electron-pair donor (OH^- , CN^- , NH_3) that attacks a $\delta+$ carbon. An **electrophile** is an electron-pair acceptor (Br_2 , H^+) that accepts a pair from an electron-rich region such as a C=C double bond. In the substitution of bromoethane, OH^- donates its pair to the $\delta+$ carbon while Br^- leaves with the bonding pair: $\text{CH}_3\text{CH}_2\text{Br} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Br}^-$.
- heterolytic fission: Bond breaking where one atom takes both shared electrons; nucleophile: An electron-pair donor attracted to a positive or $\delta+$ centre; electrophile: An electron-pair acceptor attracted to an electron-rich region.

Heterolytic fission: the PAIR moves to one atom



Nucleophilic substitution: OH^- attacks bromoethane



Nucleophile = electron-pair donor; electrophile = electron-pair acceptor

Double-barbed arrows move an electron PAIR

In heterolytic fission the pair goes to one atom; OH^- donates a pair to the $\delta+$ carbon and Br^- leaves

■ Choose evidence that can test it

- The reaction rate depends on the concentrations of BOTH bromoethane and hydroxide, supporting a mechanism in which both meet in the key step. Bromide ions appear in solution as the alcohol forms, matching the leaving-group prediction.
- Bromine water loses its orange colour with an alkene but not with the corresponding alkane – evidence that the electron-rich C=C is what attracts the electrophile.

■ Work from known quantities

- Known: $\text{Mr}(\text{CH}_3\text{CH}_2\text{OH}) = 46$; $\text{Mr}(\text{CH}_3\text{CH}_2\text{Br}) = 109$; $\text{Mr}(\text{OH}^-) = 17$. Atom economy measures how much reactant mass ends in the desired product: atom economy = $\text{Mr}(\text{desired product}) / \Sigma \text{Mr}(\text{all reactants}) \times 100\%$. Substitution: $46 / (109 + 17) \times 100\% = 46/126 \times 100\% = 36.5\%$. Substitution reactions have low atom economy because the leaving group carries mass away.

Example:

Chloroethane has $\text{Mr} = 64.5$. Find the atom economy of $\text{CH}_3\text{CH}_2\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Cl}^-$ using the same sequence: known quantities $\rightarrow$ model $\rightarrow$ relation $\rightarrow$ substitution $\rightarrow$ unit and interpretation. (Answer: $46 / (64.5 + 17) \times 100\% = 46/81.5 \times 100\% = 56.4\%$ – a lighter leaving group raises the atom economy, though it is still far below an addition reaction's 100%.)

■ Check the conclusion and its limits

- The arrow-pushing model shows electron flow in the key step; real rates also depend on the solvent and temperature, which this scheme does not capture. Atom economy compares routes on paper; a full process evaluation needs yield, energy and safety data too.

Warn:

A nucleophile is a negative ion, so any negative ion is a nucleophile and any positive species is an electrophile. This claim is false: the definition is about electron-PAIR donation – neutral NH_3 is a nucleophile because it carries a lone pair, and Br^- is a leaving group, not an attacking nucleophile, in this substitution.

Key:

Electron-pair sharing reactions: heterolytic fission moves both shared electrons to one atom; double-barbed arrows track electron pairs. Nucleophiles donate pairs to $\delta+$ centres and electrophiles accept pairs from electron-rich regions; substitution and addition mechanisms follow from that flow.